Fabrication of Carbon Nanotube Reinforced Alumina Matrix Nanocomosite by Sol-gel Process

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Abstract
Carbon nanotube reinforced alumina matrix nanocomposite was fabricated by sol-gel process and followed by spark plasma sintering process. Homogeneous distribution of carbon nanotubes within alumina matrix can be obtained by mixing the carbon nanotubes with alumina sol and followed by condensation into gel. The mixed gel, consisting of alumina and carbon nanotubes, was dried and calcinated into carbon nanotube/alumina composite powders. The composite powders were spark plasma sintered into carbon nanotube reinforced alumina matrix nanocomposite. The hardness of carbon nanotube reinforced alumina matrix nanocomposite was enhanced due to an enhanced load sharing of homogeneously distributed carbon nanotubes. At the same time, the fracture toughness of carbon nanotube reinforced alumina matrix nanocomposite was enhanced due to a bridging effect of carbon nanotubes during crack propagation.

Keywords: Carbon nanotube, alumina, nanocomposite, sol-gel process, spark plasma sintering

1. Introduction

Carbon nanotubes have opened up new technological areas to overcome the limit of conventional materials since their first discovery at 1991[1]. One of the application areas for carbon nanotubes could be a reinforcement for composite materials owing to their extra-ordinary properties such as excellent Young's modulus, good flexibility[2], low density[3], and thermal high conductivity [4].

However, carbon nanotubes tend to be agglomerated each other owing to a strong van der Waals attractive force. Therefore, it is difficult to avoid the agglomeration of carbon nanotubes during the fabrication of carbon nanotube reinforced metal or ceramic matrix nanocomposites. There have been several attempts to fabricate carbon nanotube reinforced ceramic matrix nanocomposites. However, the carbon nanotube/ceramic nanocomposite developed up to now showed much lower mechanical properties than expected. In most cases, the addition of carbon nanotubes as reinforcement improved the fracture toughness, however, on the other hand, it degraded the hardness or strength. It is mainly due to the agglomeration of carbon nanotubes and the weak interface between carbon nanotubes and the matrix.

Alumina is one of the most widely used ceramic materials owing to its relatively high hardness (15~22GPa), good oxidation resistance and chemical stability with iron or steel[5]. However, applications have been limited due to its low fracture toughness. Thus, there have been many efforts to make tougher alumina by addition of nano-sized second phases or by using a new sintering process such as spark plasma sintering[6]. In this study, carbon nanotubes are used as reinforcements to increase the fracture toughness of alumina. Sol-gel process is used to disperse carbon nanotubes homogeneously in alumina matrix by entrapping the dispersed carbon nanotubes in the gel network. The fracture toughness and hardness of carbon nanotube reinforced alumina matrix were characterized.

2. Experimental

2.1. Fabrication of carbon nanotube reinforced alumina composite powders by sol-gel process

Aluminum tri-sec-butoxide ($Al(OBu^s)_3$) was used as a precursor of alumina. The muli-wall carbon nanotubes by CVD using alumina supported catalyst have dimension of 15~30nm in diameter, 10~50μm in length and the density of 1.6(g/cm^3). Alumina sol was synthesized by Yoldas' process, which consists of hydrolysis(at 80°C)and peptization of aluminum hydroxide(AlOOH)[7, 8]. The carbon nanotubes dispersed in form of suspension within ethanol was added to alumina sol during the gelation process. The volume fraction of carbon nanotubes was controlled as 0%, 1.5% and 3.3%. The carbon nanotube/alumina gel was dried at 350°C for 6hrs. The carbon nanotube/alumina composite powders were fabricated by calcinations of gel powder at 1250°C for 1hour in vacuum of 10Pa.

2.2. Consolidation and characterization of carbon nanotube reinforced alumina matrix nanocomposites

Calcinated carbon nanotube/alumina powders were loaded in graphite mold and followed by spark plasma sintering at 1650°C for 5min. under applied pressure of 25MPa. Spark plasma sintered carbon nanotube/alumina was annealed at 1000°C for 6hrs to remove carbon diffused from the graphite mold. The hardness of carbon nanotube reinforced alumina matrix nanocomposite was measured using Vicker's indentation test under a load of 9.8N and the fracture toughness was evaluated by measuring the crack length generated by Vicker's indentation.

3. Results and discussion

The XRD analysis in Fig. 1(a) shows that α-alumina was formed during the calcinations process of alumina gel. The analysis result of FT-IR(EQUINOX 55) in Fig. 1(b) shows that there were no apparent additional peaks from the bond at the interface between alumina and carbon, which is known to be located at 605cm^{-1} and 802cm^{-1}[9]. This indicates the carbon nanotubes are stable at elevated temperature during the calcinations.

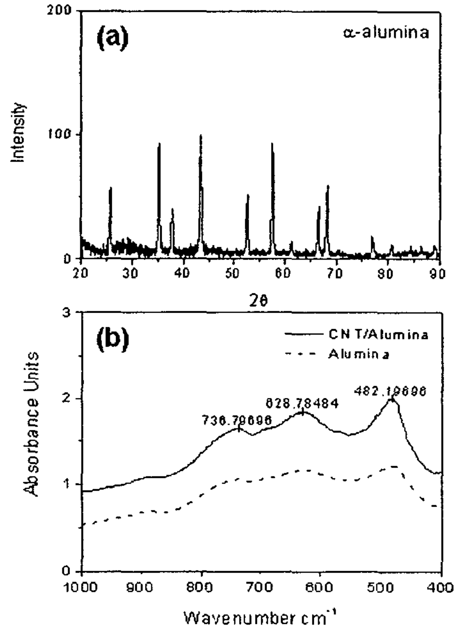

Figure 1. (a) The XRD analysis and (b) FT-IR analysis of calcinated carbon nanotube/alumina composite powders.

The relative density of carbon nanotube/alumina nanocomposite fabricated by consolidating the composite powders using spark plasma sintering is varied from 99.5% to 100% regardless the volume fraction of carbon nanotubes. Fig. 2 shows the fractured surface of carbon nanotubes reinforced alumina nanocomposite fabricated by the sol-gel process and followed by spark plasma sintering. The pulled-out carbon nanotubes were shown

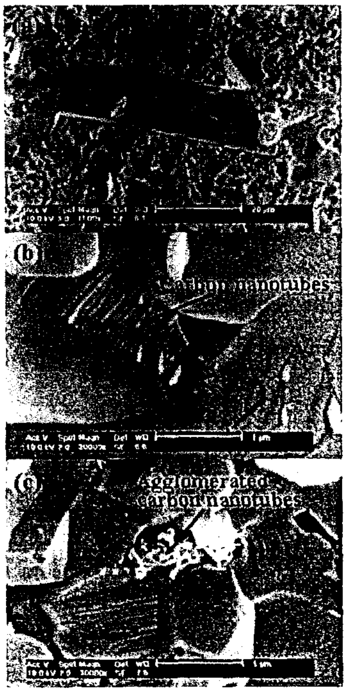

Figure 2. The SEM micrographs of fractured surface of carbon nanotube/alumina nanocomposite fabricated by sol-gel process and followed by spark plasma sintering with varying the volume fractions of carbon nanotubes. The volume fraction of carbon nanotube is (a) 0%, (b)1.50% and (c) 3.0%.

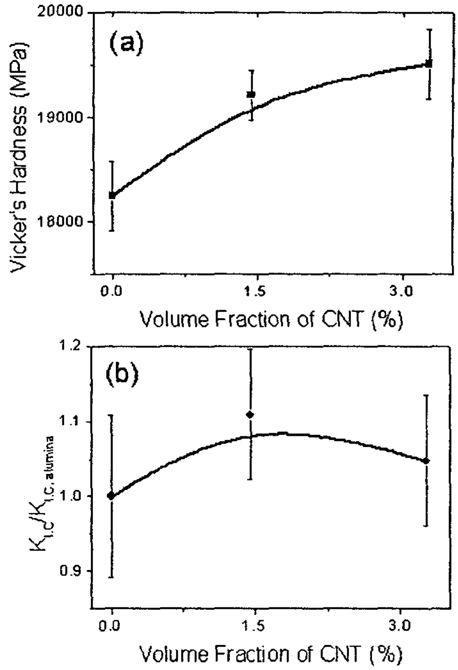

Figure 3. (a) Hardness and (b) fracture toughnes of carbon nanotubes/alumina nanocomposite, normalized by that of monolithic alumina, with varying the volume fraction of carbon nanotubes.

on the fracture surface of carbon nanotube/alumina nanocomposite. It shows that the interface between carbon nanotube and alumina matrix is strongly bonded and a significant load transfer occurs from the matrix to carbon nanotubes during the loading. One thing to notice in microstructure is that some carbon nanotubes are reinforced within the alumina grains as shown in Fig. 2(b). However, when the volume fraction of the carbon nanotube increases up to 3.3%, some carbon nanotubes become agglomerated shown on the fractured surface of carbon nanotube/alumina composite as shown in Fig. 2(c).

Fig. 3 shows the mechanical properties, including hardness and fracture toughness, of carbon nanotube/alumina nanocomposites fabricated by sol-gel process and followed by spark plasma sintering process.

The hardness of carbon nanotube/alumina nanocomposite increases with increasing the volume fraction of carbon nanotubes. This result is much different from the previous reports that the hardness of carbon nanotube reinforced alumina matrix nanocomposites decreases with increasing the volume fraction of carbon nanotubes [10]. It is mainly due to a difference in distribution of carbon nanotubes within the alumina matrix and interfacial strength between carbon nanotube and alumina matrix. In previous research, the carbon nanotubes were generally agglomerated, hence the load transfer from the matrix to carbon nanotube could not be high[10, 11, 12]. However, in this study, the carbon nanotubes were dispersed within the alumina grains and strongly bonded with the alumina matrix, as shown in Fig. 2. Therefore, the effective load transfer from the matrix to carbon nanotube is possible, and a significant load sharing of carbon nanotubes mainly enhances the hardness of carbon nanotube/alumina nanocomposites. This is also shown in carbon nanotube reinforced polymer nanocomposites, whose strength can be improved by about 10 times with reinforcing carbon nanotubes in polymer matrix[13]. The fracture toughness of carbon nanotube reinforced alumina matrix nanocomposite was enhanced compared to that of monolithic alumina. The fracture toughness of carbon nanotube/alumina nanocomposite containing 1.5 vol.% of carbon nanotubes was 10% higher than that of monolithic alumina. However, when the volume fraction of carbon nanotubes increased to 3.3%, the fracture toughness decreases slightly, however maintain higher toughness than monolithic alumina. This is mainly due to a presence of residual pores located between the agglomerated carbon nanotubes in nanocomposites as shown in Fig. 2(c). The toughening mechanism in carbon nanotube/alumina nanocomposite fabricated by the sol-gel process can be explained by a crack bridging effect of carbon nanotubes. The carbon nanotubes, which bridge the two crack surfaces as shown in Fig. 4, strongly supports the crack bridging effect during the crack propagation. When some carbon nanotubes are agglomerated, the fracture toughness decreases due to a decrease in crack bridging effect of carbon nanotubes as shown in carbon nanotube/alumina nanocomposite containing 3.3vo.% of carbon nanotubes.

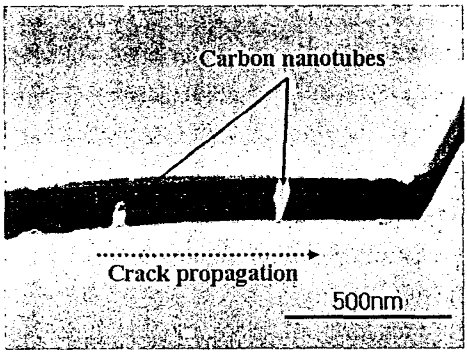

Figure 4. The micrographs showing the bridging effect of carbon nanotubes during crack propagation, which is observed after Vicker's indentation of carbon nanotube/alumina nanocomposite.

4. Conclusions

The carbon nanotubealumina nanocomposite with enhanced hardness and fracture toughness was successfully fabricated by sol-gel process and followed by spark plasma sintering. The carbon nanotubes were homogeneously dispersed within alumina matrix in carbon nanotube/alumina nanocomposite. The hardness and fracture toughness of carbon nanotube/alumina nanocomposites enhanced with increasing the volume fraction of carbon nanotubes. The strengthening mechanism is based on the load transfer between the alumina matrix and carbon nanotubes. The toughening mechanism is strongly related to the crack-bridging effect of carbon nanotubes during the crack propagation in carbon nanotube/alumina nanocomposites.

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